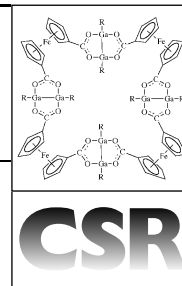


# Organogallium(II) compounds bearing chelating ligands, bridging versus terminal co-ordination of gallium–gallium single bonds



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Received 13th March 2000

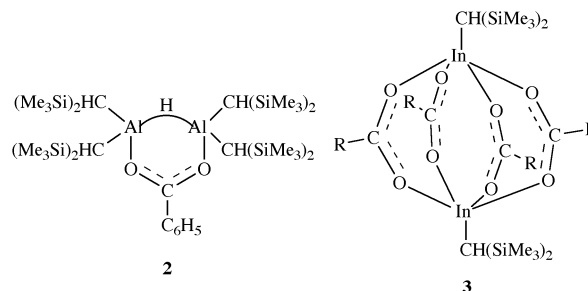
Published on the Web 8th June 2000

**Tetrakis[bis(trimethylsilyl)methyl]digallane(4) 1 containing gallium atoms in an oxidation state of +II and a Ga–Ga single bond is a versatile starting compound for the synthesis of a broad variety of derivatives. One of the most exciting reactions is the substitution of alkyl groups without cleavage of the Ga–Ga bond, which succeeds by the treatment of 1 with chelating protonic acids such as carboxylic acids and acetylaceton derivatives. In all cases, two chelating ligands were introduced, which depending on their structural parameters either occupy terminal positions with each one co-ordinated to only one gallium atom or bridge the Ga–Ga bond. The reason for the different co-ordination behavior is discussed here.**

## 1 Introduction

The dielement compounds  $R_2E-ER_2$  with  $E = Al, Ga$  (**1**), or  $In$  and  $R = CH(SiMe_3)_2$  were obtained by our group about ten years ago.<sup>1–3</sup> They were the first well characterized organoelement compounds reported in the literature which contained Al–Al, Ga–Ga, and In–In single bonds. Our investigations into the reactivity of this new class of compounds revealed fascinating properties, and up to now we have observed six different types of reaction: (i) deprotonation, (ii) formation of radical anions containing  $1e-E-E \pi$ -bonds, (iii) formation of adducts, (iv)

insertion reactions, (v) substituent exchange by retention of the element–element bonds, (vi) metathesis reactions.<sup>4</sup> This article focuses on substituent exchange reactions, which by the treatment of the dielement compounds with protonic acids and the release of bis(trimethylsilyl)methane give novel dielement species. However, such reactions succeeded only when the digallium derivative **1** was employed and require acids with chelating residues. In contrast, the cleavage of the Al–Al or In–In bonds was observed whenever we treated the dialuminium or diindium analogues with a proton donor.<sup>5,6</sup> The aluminium compound and benzoic acid gave the ( $\mu$ -carboxylato)( $\mu$ -hydrido)dialuminium derivative **2** (Scheme 1), in which a  $3c-2e$



Scheme 1

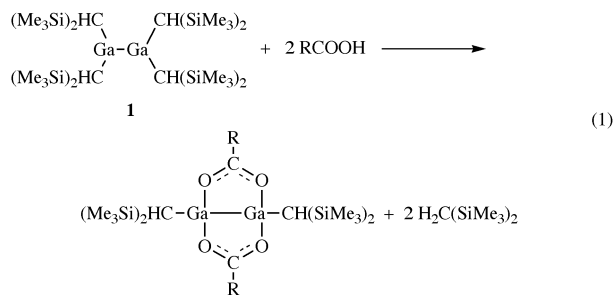
Al–H–Al bond is bridged by a carboxylato group.<sup>5</sup> Owing to the instability of the In–H bond, a similar product was not obtained by the analogous reaction of the diindium compound. Instead, two products were isolated, which were identified as  $R_2In(O_2C-C_6H_5)$  [ $R = CH(SiMe_3)_2$ ] and  $[RIn(O_2C-C_6H_5)_2]_2$  (**3**). The latter has a remarkable cage structure, in which two indium atoms are bridged by four benzoato groups (Scheme 1).<sup>5</sup> The successful substituent exchange reactions of the digallium compound **1** yielded products with coordinatively saturated gallium atoms and intact Ga–Ga bonds, in which the chelating ligands occupy either terminal or bridging positions. A systematic approach to an understanding of the different co-ordination behavior is given here.

## 2 Reactions of digallane(4) 1 with carboxylic acids

Complete consumption of compound **1** was only achieved when at least two equivalents of the carboxylic acids were added to a solution of **1** in pentane [eqn. (1)].<sup>7–9</sup> The reactions generally started under mild conditions before warming of the mixtures to room temperature. In each case, two equivalents of bis(trimethylsilyl)methane were liberated, and the products were isolated in almost quantitative yields of between 80 and 97%. Aliphatic and aromatic carboxylic acids showed no difference in their reactivity towards the digallium compound, and the steric shielding by the different carboxylato ligands has only an



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R = -C<sub>6</sub>H<sub>5</sub> (4), -4-Br-C<sub>6</sub>H<sub>4</sub> (5), -3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>2</sub> (6), -CMe<sub>3</sub> (7), -Adamantyl (8), -CH<sub>3</sub> (9)

insignificant influence on the stability of the products, as can be seen from a comparison of the adamantanecarboxylato and acetato derivatives, respectively.<sup>8,9</sup> The resonances of the carbon and hydrogen atoms of the methine groups attached to gallium are strongly shifted to a higher field compared with compound **1**, which is very indicative of an enhancement of the co-ordination number at the gallium atoms from three to four. In the IR spectra, the stretching vibration of the CO<sub>2</sub> groups is generally observed at about 1535 cm<sup>-1</sup>; only with the smallest acetato derivative does the absorption (1555 cm<sup>-1</sup>) deviate significantly from this average value. In contrast to yellow **1**, all products obtained by the reaction with acids having coordinatively saturated gallium atoms are colorless.

Three compounds were characterized by crystal structure determinations (**5**, R = *p*-bromophenyl; **8**, R = adamantyl; **9**, R = methyl),<sup>7-9</sup> the molecular structure of the acetato derivative is depicted in Fig. 1. In all cases the Ga–Ga bond is bridged by

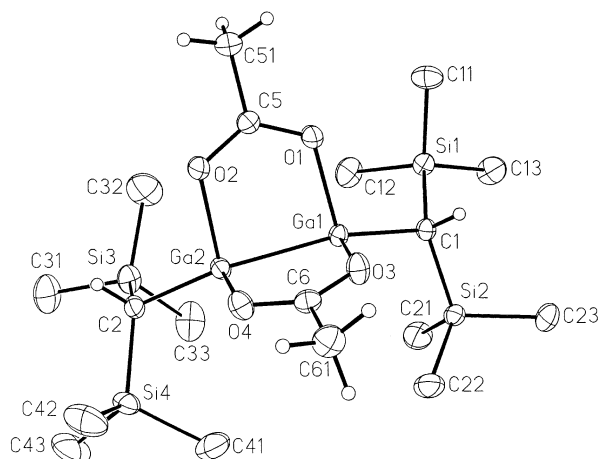
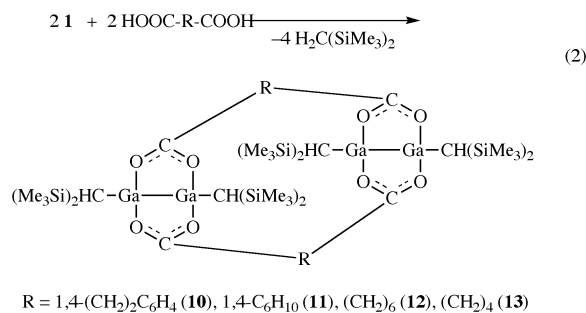


Fig. 1 Molecular structure of compound **9**; methyl hydrogen atoms are omitted for clarity.

two carboxylato ligands. While those structures were often observed in transition metal chemistry, to the best of our knowledge only two further examples are known with main group elements, which contain single bonds between boron or tin atoms.<sup>10,11</sup> The Ga–Ga bonds (237.9 to 239.1 pm) are significantly shortened compared to the starting compound **1** (254.1 pm), which may be caused by the co-ordination with electronegative oxygen atoms and the bridging by the carboxylato groups with a short distance between the co-ordinating atoms of 223.2 to 224.2 pm. The Ga–O bonds are almost perpendicular to the Ga–Ga bonds (88° on average), and the normals of the planes of both Ga<sub>2</sub>O<sub>2</sub>C heterocycles enclose angles between 91 and 94°. Thus, the bonding situation of these molecules may be described simply by the classic picture of sp<sup>3</sup>-hybridized gallium atoms, and both p-orbitals perpendicular to the Ga–Ga bond interact with the oxygen atoms of the bridging groups. Quantum chemical calculations on a formato bridged derivative verify this model,<sup>9</sup> and those orbitals of the gallium atoms which are involved in the Ga–O bonds have a strong p

character (sp<sup>6.1</sup>). Quantum chemical calculation of a molecule with terminally co-ordinated ligands gave the remarkable result that it is 117 kJ mol<sup>-1</sup> more unfavorable than the molecule with bridging groups. An important contribution to this higher energy is made by the deformation of the OCO angle from 124.7° in the bridged molecule to 116.7° for the terminally co-ordinated Ga–Ga bond (calculated for free HCOO<sup>-</sup>: 129.9°). Accordingly, even the carboxylates of the trivalent elements aluminium, gallium, and indium often form dinuclear, bridged compounds, instead of mononuclear derivatives with the central atom co-ordinated by both oxygen atoms of only one ligand.<sup>12</sup>

Treatment of the tetraalkyldigallium compound **1** with dicarboxylic acids is a very effective method for the synthesis of macrocycles. According to eqn. (2), the reaction of **1** with



benzene-1,4-diacetic acid, cyclohexane-1,4-dicarboxylic acid, hexane-1,6-dicarboxylic acid, and butane-1,4-dicarboxylic acid (adipic acid) gave macrocycles with up to 22 atoms in excellent yields of 83 to 86%, in which the dicarboxylato groups bridge two digallium moieties.<sup>8</sup> Two of the products (**10** and **11**) were characterized by crystal structure determinations; the structure of the cyclohexanediyl bridged compound (**11**) is depicted in

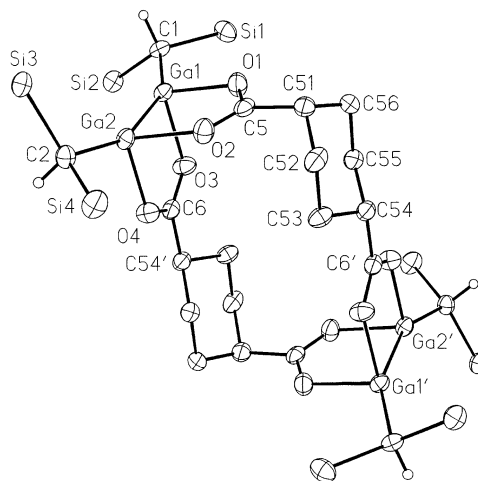
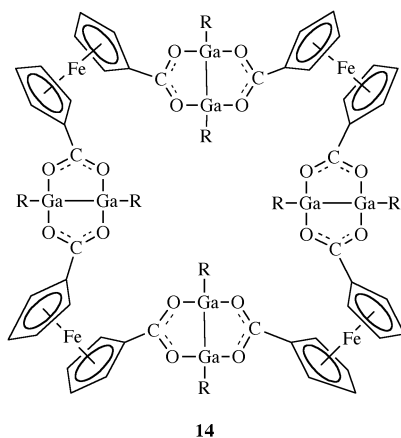


Fig. 2 Molecular structure of compound **11**; methyl groups and hydrogen atoms of the C<sub>6</sub>H<sub>10</sub> bridge are omitted for clarity.

Fig. 2. As described before, the short Ga–Ga bonds (237.5 to 238.3 pm) are bridged by carboxylato ligands, the Ga–Ga–C groups approach linearity (about 155°), and the chelating groups stand almost perpendicular to one another.

An even larger heterocycle (**14**) containing 32 atoms was formed in 85% yield when **1** was treated with the more rigid ferrocenedicarboxylic acid. As schematically shown in Scheme 2, the heterocycle comprises four Ga–Ga bonds and four ferrocenedicarboxylato groups.<sup>13</sup> Thus, these reactions are powerful methods for the syntheses of macrocyclic compounds, and we hope to introduce donor atoms and to use these derivatives as macrocyclic ligands, for instance. But there are limitations to such reactions, and no pure products were isolated with maleic acid, benzene-1,2- and -1,4-dicarboxylic acid, 4,4'-

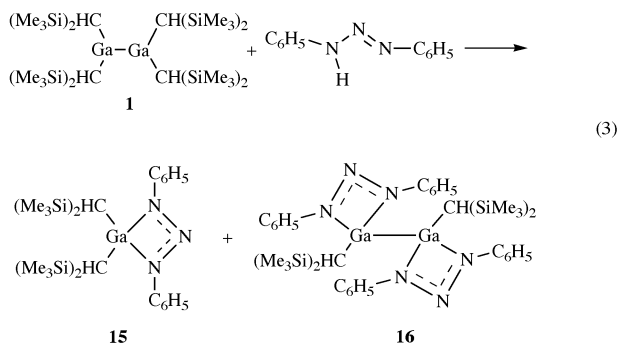


Scheme 2

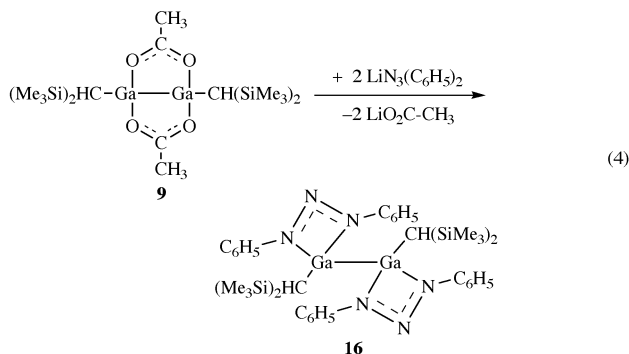
oxybis(benzoic acid), and 2,2-dimethylpropane-1,3-dicarboxylic acid.<sup>8</sup>

### 3 Reactions of 1 with very weak proton donors

Very weak acids with monodentate residues gave cleavage of the Ga–Ga bond in all cases.<sup>6</sup> But even with chelating residues an at least partial cleavage of the metal–metal bond was observed. The most well-known reaction of this type is that of **1** with diphenyltriazene Ph<sub>2</sub>N<sub>3</sub>H [eqn. (3)]. Two products were



formed in a molar ratio of 7 : 3, which could not be separated by recrystallization.<sup>14</sup> The two compounds differ slightly in their colors (yellow, **15**; yellow–orange, **16**), and we succeeded in isolating small quantities of the pure components by manual sorting of the large crystals under a microscope. They were easily identified as **15**, which was the main product and resulted from cleavage of the Ga–Ga bond, and the digallium compound **16**, which is the expected product of a substituent exchange reaction. As was shown by NMR spectroscopy and in particular by the characteristic chemical shifts of the atoms of the methine groups, the gallium atoms of **16** are co-ordinated by the triazenido ligand in a chelating manner. As will be described in the next section [eqn. (4)], we meanwhile found a different, facile route for the synthesis of pure **16** in high yield.



As depicted in Fig. 3, **16** adopts a different configuration compared with the carboxylato derivatives. The Ga–Ga bond is

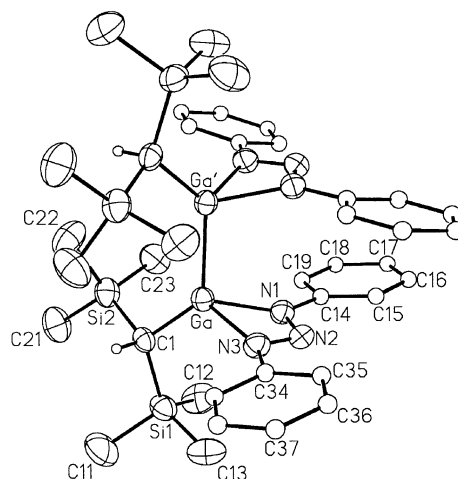


Fig. 3 Molecular structure of compound **16**; most hydrogen atoms are omitted for clarity.

not bridged by the chelating ligands, but the triazenido groups occupy terminal positions at each gallium atom.<sup>14</sup> The molecule resides on a crystallographic twofold rotation axis with an approximate *cis* arrangement of the substituents. The molecular halves are, however, not exactly synperiplanar, but twisted with a torsion angle C–Ga–Ga–C of 45.1°. The Ga–Ga bond length (245.8 pm) is shorter than that of compound **1** (254.1 pm), but longer than the average value observed for the carboxylato derivatives (238 pm). This relaxation may be caused by the lower electronegativity of the nitrogen atoms and the terminal co-ordination of the gallium atoms, so that the Ga–Ga bond length is no longer affected by the bite of the chelate.

The most remarkable observation is the different behavior of the ligands with bridging *versus* terminal co-ordination. The smaller bite of the triazenido ligand may be discussed as a reason, but as will be shown later on, the triazenido group can easily be forced to bridge the Ga–Ga bond. Quantum chemical calculations showed that, in comparison with the carboxylato ligand, the triazenido group is more suitable for terminal co-ordination with a more relaxed, distorted tetrahedral co-ordination sphere at the gallium atoms, and many compounds are known from the literature with terminally co-ordinated aluminium, gallium, or indium atoms.<sup>14,15</sup> The N–N–N angle calculated for the free triazenido anion is 114.6°, which is intermediate between that observed for the bridging (116.8°, see below) and for the terminally co-ordinated triazenido group (105.9°). The energy difference between the two situations was calculated to be only 13 kJ mol<sup>−1</sup>.<sup>9</sup> Thus, the energy required for the deformation of the NNN group is lower and the bond angle in the ground state is smaller than the corresponding values detected for the carboxylato ligand.

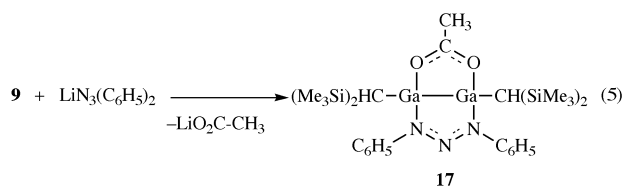
### 4 Syntheses of further compounds starting with di(μ-acetato)digallium 9

As shown above, substituent exchange by retention of the Ga–Ga bond is restricted to relatively strong acids such as carboxylic acids. Very weak proton donors give partial or complete cleavage of the element–element bond with the formation of mononuclear gallium derivatives. In order to get a better insight into the different co-ordination behavior of chelating ligands, it was of particular interest to find another, more effective route for the synthesis of such digallium compounds. The easily available dicarboxylato derivatives

seemed to be suitable starting materials, because they should allow substitution reactions upon treatment with appropriate lithium compounds, which may be favored by the precipitation of sparingly soluble lithium carboxylates. Due to its low steric shielding, we exclusively employed the diacetato derivative **9**, and started with some reactions which should yield well-known products. In most cases, the diacetato derivative was not isolated and purified, but treated *in situ* with the corresponding lithium reagent.

A simple reaction was the treatment of **9** with two equivalents of bis(trimethylsilyl)methyl lithium, which gave the tetraalkyl-digallium compound **1** in an overall yield of 51%.<sup>9</sup> Although a trivial reaction, it showed that compound **9** is suitable for the synthesis of further digallium compounds containing different substituents attached to their gallium atoms. In a second reaction, **9** was treated with lithium diphenyltriazenide in a molar ratio of 1:2 [eqn. (4)], which gave the bis(diphenyltriazenido) derivative **16** in a yield of 86% based on **1**. As described above [eqn. (3)], **16** was isolated previously only in a mixture with the mononuclear cleavage product **15**.

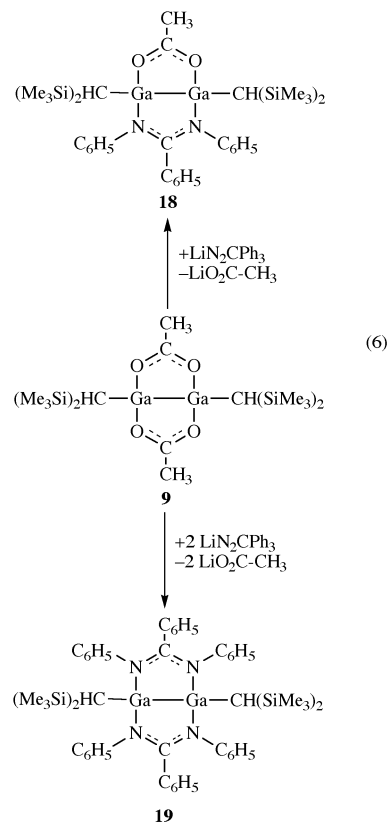
In order to obtain digallium compounds containing different chelating ligands, we were much interested in replacing only one of the acetato groups. Such derivatives are useful as starting materials and contain gallium atoms in a chiral environment. Furthermore, they allow the systematic investigation of the resulting molecular structures, if ligands with competing preferences for the mode of co-ordination are present. Therefore, we treated the diacetato compound **9** with lithium diphenyltriazenide in a stoichiometric 1:1 ratio and isolated the acetato triazenido compound **17** in a yield of 80% [eqn. (5)]. In



contrast to the bis(triazenido) derivative **16** with an exclusively terminal arrangement of the chelating ligands, the triazenido group in **17** occupies a bridging position, which clearly is caused by the high tendency of the carboxylato group to bridge the Ga-Ga bond. The Ga-Ga bond length (236.8 pm) and the structural parameters of the Ga<sub>2</sub>O<sub>2</sub>C heterocycle are similar to those of the previously discussed carboxylato derivatives, but large differences occur for the triazenido group in comparison with the terminally co-ordinated ligand of compound **16**. The N-N-N angle is enlarged to 116.8° compared with the much smaller angle of 105.9° of **16**, which leads to a larger bite between the two co-ordinating nitrogen atoms of 221.6 pm (209 pm in **16**) similar to that of the carboxylato group (224.4 pm). Both gallium atoms possess a chiral co-ordination sphere, which results in an *R* and *S* configuration, but the whole molecule is non-chiral due to a mirror plane perpendicular to the Ga-Ga bond and adopts the *meso* structure. The remaining structural parameters are similar to those discussed before. The C-Ga-Ga-C group is almost linear (angle Ga-Ga-C 152.6°), and the bridging groups are almost perpendicular to one another (91.0°). Owing to the molecular symmetry the trimethylsilyl groups become diastereotopic and give two resonances of equal intensity in the NMR spectra.

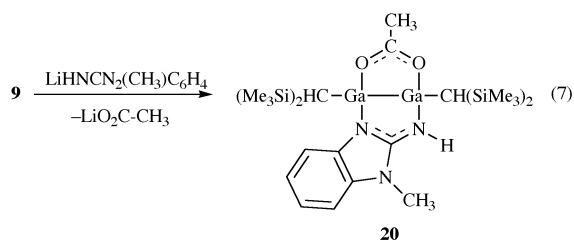
In order to systematically change the co-ordination properties of the chelating ligands, we replaced the central nitrogen atom of the triazenido group by a carbon atom and reacted lithium diphenylbenzamidinate with the diacetato compound **9**.<sup>9</sup> Owing to the long C-N distances and the large bond angle at the inner carbon atom, a bridging co-ordination of the Ga-Ga bond was predicted. Only the product of the replacement of one acetato group (**18**) was obtained in a pure and crystalline form and was characterized by a crystal structure determination

[eqn. (6)], while the bis(benzamidinato) derivative **19** was isolated as an oily residue, which could not be purified by



recrystallization. The molecular structure of **18** is similar to that of compound **17** with two chiral molecular halves and an overall *meso* configuration. The Ga-Ga bond is short (236.7 pm), and the angles Ga-Ga-C approach linearity (153.9°). The angle between the planes Ga<sub>2</sub>O<sub>2</sub>C and Ga<sub>2</sub>N<sub>2</sub>C is 93.1°. The Ga-N distances observed for **18** are shorter than those of **17** (201.7 compared to 206.2 pm), which in accordance with the large bond angle at the central atom of the bridging ligand (120.8 compared to 116.8°) and the large bite between the co-ordinating atoms (230.9 compared to 221.6 pm) may be caused by the lower steric stress in the benzamidinato compounds. Although the bis(benzamidinato) derivative **19**, eqn. (6), was not characterized by a crystal structure determination, we suppose that owing to the particular geometrical parameters of the benzamidinato groups its Ga-Ga bond may also be bridged by the chelating ligands.

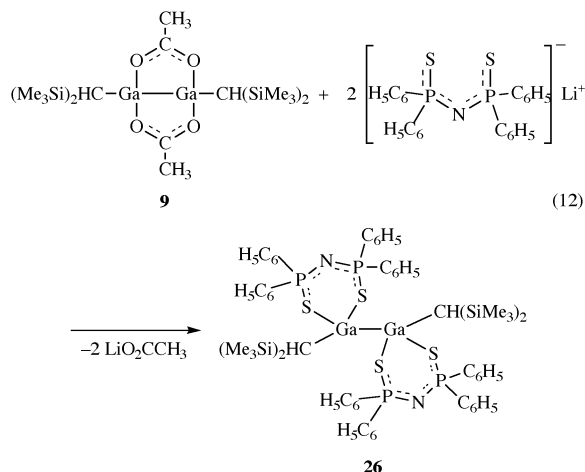
Up to now only ligands possessing a mirror plane perpendicular to the molecular axis have been employed. But owing to the formation of *meso* compounds such as **17** or **18** containing gallium atoms in a chiral environment, we were much interested in the introduction of more asymmetric ligands, in order to reduce the molecular symmetry. Therefore, we treated the diacetato derivative **9** with lithium 2-amino-1-methylbenzimidazolone and isolated the (acetato)(benzimidazolato)digallium compound **20** in a yield of about 50% [eqn. (7)]. As expected



from the large bite of the benzimidazolato ligand, the Ga-Ga bond (240.1 pm) is bridged by both chelating groups.<sup>16</sup>

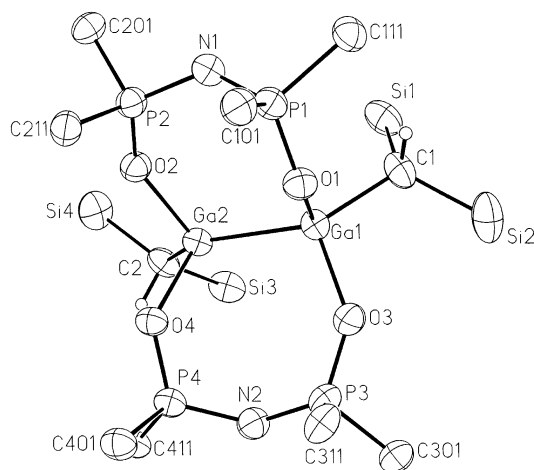


was formed by cleavage of the Ga–Ga bond, while the second one (**25**) resulted from a substituent exchange reaction. The two products were easily separated by recrystallization. In contrast, probably owing to insufficient  $\pi$  delocalization in its anion the sulfur derivative imidotetraphenyldithiodiphosphinic acid is such a weak proton donor that only a mixture of several unknown compounds was formed, from which the product of a substituent exchange (**26**) was isolated in trace amounts. **26** was isolated in a yield of 55%, when we treated the diacetatodigallium derivative **9** with the lithium salt of the dithio compound [eqn. (12)].<sup>18</sup> Owing to their molecular symmetry,



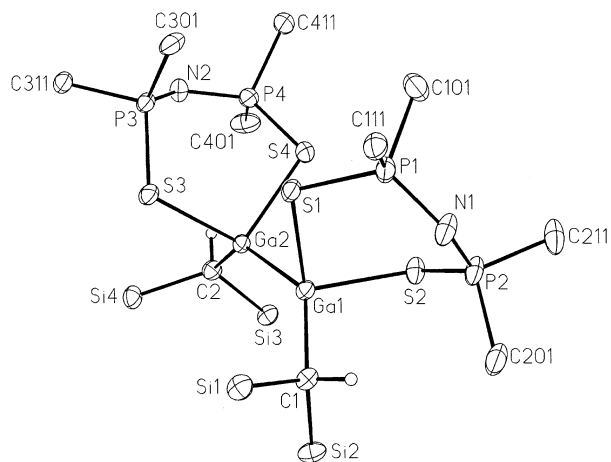
the two digallium compounds **25** and **26** possess chemically different phenyl groups. Only one sort shows a coupling of the *ipso* carbon atom to both phosphorus atoms of the ligand, which according to the Carplus–Conroy equation can be correlated nicely with the torsion angles in the PNPC groups.

Despite their great similarity, the two digallium compounds



**Fig. 4** Molecular structure of compound **25**; methyl and phenyl groups without the *ipso* carbon atoms are omitted for clarity.

(**25** and **26**) adopt different structures (Figs. 4 and 5). Bridging of the Ga–Ga bond is observed for the oxygen compound **25**, while the dithio ligands occupy terminal positions. Thus, in the first case two annellated seven-membered heterocycles were obtained, while in the second two six-membered heterocycles were obtained, which are connected by the Ga–Ga bond. As expected, the Ga–Ga distance is a little longer in the terminally co-ordinated derivative **26** (249.9 compared to 245.6 pm). As in the carboxylato compounds, the chelating ligands in the bridged compound **25** are almost perpendicular to one another (angles OGaO 93.6° on average), but the C–Ga–Ga–C groups deviate



**Fig. 5** Molecular structure of compound **26**; methyl and phenyl groups without the *ipso* carbon atoms are omitted for clarity.

more from linearity with GaGaC angles of 135.5°. The free acids have different structures. The oxygen derivative possesses the OH form with a delocalized electronic  $\pi$  system,<sup>19</sup> while the hydrogen atom is located at the nitrogen atom in the sulfur derivative.<sup>19–21</sup> Different P–N distances of 153.5 and 168 pm, respectively, result from these different bonding situations. In accordance with the occurrence of a delocalized  $\pi$  system in the two digallium compounds **25** and **26**, the P–N distances are almost identical (159 pm). For the same reason, the P–O separation in **25** is similar to that of the free acid (151.8 pm), while the P–S distance is lengthened from 194 pm in the N–H compound to 202.7 pm in **26**.

The bites of both ligands are similar (O–O, 367.5 pm; S–S, 370.1 pm), so that consideration of only the distance between the co-ordinating atoms clearly is not sufficient for understanding their different coordination modes. The main difference between the two structures is observed for the angles Ga–O–P (129 to 143°) and Ga–S–P (103 to 107°). To some degree, this may reflect the more covalent bonding character of the Ga–S compared to the Ga–O bond, but these observations are also in accordance with the low tendency of sulfur for hybridization. Owing to the short Ga–O distances, the terminal co-ordination of chelating oxygen ligands requires bites shorter than 300 pm. Such a short distance is realized in the acetylacetonato derivatives with short C–C bonds (see **23** with an O–O distance of 278.9 pm), but it requires a deformation of the angles in the imidotetraphenyldiphosphinato ligand with relatively long P–N bonds, so that the bridging of the Ga–Ga bond may be favored. In contrast, the longer Ga–S bonds allow terminal co-ordination, and the bite of 370 pm observed in **26** and several mononuclear compounds<sup>22</sup> can be realized without a dramatic deformation of the central P–N–P angle.

## 6 Conclusion

It is a quite remarkable fact that substituent exchange reactions can be realized by the treatment of the tetraalkyldigallium compound **1** with protonic acids by retention of the Ga–Ga bond. In contrast and as expected, complete cleavage of the Al–Al and In–In bonds was observed whenever we treated the corresponding aluminium or indium derivatives with proton donors. Successful exchange reactions with the digallium compound require large substituents for the steric shielding of the products or the introduction of strongly chelating ligands for the co-ordinative saturation of the gallium atoms. Two types of products were isolated and characterized, which have the chelating ligands either in a terminal or a bridging position. The

co-ordination behavior of the three-atomic ligands is determined by the angle at their central atoms. A terminal co-ordination with a relaxed bonding situation around the gallium atoms needs small angles, which can be realized by the triazenido ligand, for instance. Carboxylato groups and related systems have large central angles, their deformation is energetically unfavorable, and they prefer to occupy bridging positions over the Ga–Ga bond. Also with five-atomic ligands, the cooperative effect between the bite necessary for a particular co-ordination mode, the lengths of the bonds to the gallium atoms, and the energy required for the deformation of the angles seem to determine the structure finally observed.

The substituent exchange reactions reported here mark only the beginning of intensive future investigations into the chemical properties of compounds containing Ga atoms with an oxidation state of +II. They showed that the Ga–Ga bond is a very effective building block for molecular self-assembly processes and for the preparation of macrocycles. This may be helpful for the synthesis of novel macrocyclic Lewis bases, for the formation of co-ordination compounds, and for studying molecular self-organization. But also the formation of polymers or dendrimers will be a reasonable goal of future investigations. These reactions are suitable for the facile synthesis of products with high concentrations of heteroatoms such as nitrogen, similar to compound **16**, sulfur, selenium *etc.* from which the preparation of solid materials may succeed. Furthermore, compounds such as the diacetato derivative **9** may be facile starting materials for the synthesis of new cluster compounds containing gallium in an oxidation state lower than +II, or they may be employed to form bonds between transition metals and gallium. The last two points have attracted considerable interest in recent literature.

## 7 Acknowledgements

I am very grateful to my co-workers in this project for their very engaged work: Lars Cuypers, Dr Ingo Hahn, Kristiane Schüler, and Dr Thomas Spies. I should also like to thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen In-*

*dustrie* for generous financial support of the work reported herein.

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